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## Reaction of Iodine Vapor with Vacuum-Deposited Metal Films

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Weight gains due to the iodination of silver, copper, and lead films have been measured in the temperature range from 25 to 300°C with quartz crystal oscillator microbalance. Below 200°C, the iodination of silver obeys the parabolic rate relationship and its rate decreases with increasing temperature. Above 200°C, the iodination obeys the linear relationship and its activation energy is roughly estimated to be 5 kcal/mol. In the iodination of copper, the parabolic reaction with an activation energy of 3.9 kcal/mol prevails below 150°C, and the linear reaction, whose rate decreases with increasing temperature, prevails above 150°C. The iodination of lead approximately obeys the parabolic relationship and its activation energy is 13.9 kcal/mol.

### I. INTRODUCTION

Tammann<sup>1)</sup> and Tammann and Köster<sup>2)</sup> found the parabolic rate relationship in early studies of the reaction of gases with metals. They also found that the iodination of silver, copper, and lead was independent of temperature except that the rate constant rose suddenly at the transformation temperature of iodide. There have been very few studies of the halogenation of such metals since,<sup>3-6)</sup> and such peculiar reactions which do not obey Arrhenius's equation are still unclear<sup>7)</sup> and await explanation.<sup>8)</sup> The early method for measuring film thickness by color effects was not very accurate. Much more accurate experimentation, therefore, is required for a clear understanding of the halogenation mechanism.

We previously developed quartz crystal oscillator microbalance techniques for the studies of chemical reactions.<sup>9,10)</sup> In the present paper, the measurement of weight gain through the course of the reaction with time is represented for the iodination of silver, copper, and lead films, and the mechanisms of the reactions are discussed. A part of this work has been published in separate papers.<sup>11-15)</sup>

### II. EXPERIMENTAL

AT-cut quartz plates with 3.58-MHz resonance frequency, whose sensitivity for mass determination is  $2.89 \times 10^7$  Hz/(g/cm<sup>2</sup>), were used as the crystal oscillators of a microbalance.<sup>9)</sup> Several thousand Å thick films of silver (99.99%), copper (99.999%), and lead (99.99%) were prepared by vacuum-deposition onto one of the gold electrodes of the quartz plates in a vacuum of  $5 \times 10^{-7}$  Torr or less. In the experiments at temperatures above 150°C, the specimen films were directly deposited onto one surface of the plates,

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without gold, and simultaneously used as one of the electrodes, since the gold electrodes, when in contact and alloyed with the specimen metals, were appreciably attacked by iodine vapor at higher temperature. The reaction chamber in which the quartz plate was placed was temperature-controlled within  $\pm 0.5^\circ\text{C}$  of a given temperature, and iodine gas was introduced into it. The mass change during the reaction was continuously measured with the recording quartz crystal oscillator microbalance.<sup>14)</sup> The oscillator plates were vibrated at an exciting power of about 5 mW, and the vibration had no appreciable influence on the reaction.<sup>15)</sup>

### III. RESULTS

#### Reaction of Iodine Vapor with Silver Films

Good reproducibility was usually obtained for various weight measurements at a given temperature and pressure. Some weight gain/time curves for the iodination of silver below  $150^\circ\text{C}$  are reproduced in Fig. 1. The reaction product was the  $\beta$ -form (wurtzite type) crystals. The scales of  $\mu\text{m}$ , for the mean thickness of the iodide layer, and of  $\text{mg}/\text{cm}^2$ , for the weight gain, are also presented. The reaction rate decreases with increasing temperature up to  $125^\circ\text{C}$ . Since the double logarithmic plots fall on straight lines with a gradient of about  $1/2$  and the square plots also lie on nearly straight lines, it is concluded that the iodination of silver in the  $\beta\text{-AgI}$  phase region approximately obeys the parabolic rate relationship. The reaction rate increases abruptly at  $150^\circ\text{C}$ . This is caused by the formation of the  $\alpha$ -form of silver iodide whose transformation temperature is  $146^\circ\text{C}$ , as Tammann and Köster pointed out.<sup>2)</sup> The reaction at  $140^\circ\text{C}$  gave a transitional curve. At its initial stage the reaction is similar to that at  $150^\circ\text{C}$ . At a reaction time of about 10 sec the rate decreases rapidly and thenceforth the reaction seems to follow a parabolic relationship similar to that for the reaction at  $125^\circ\text{C}$  and below.

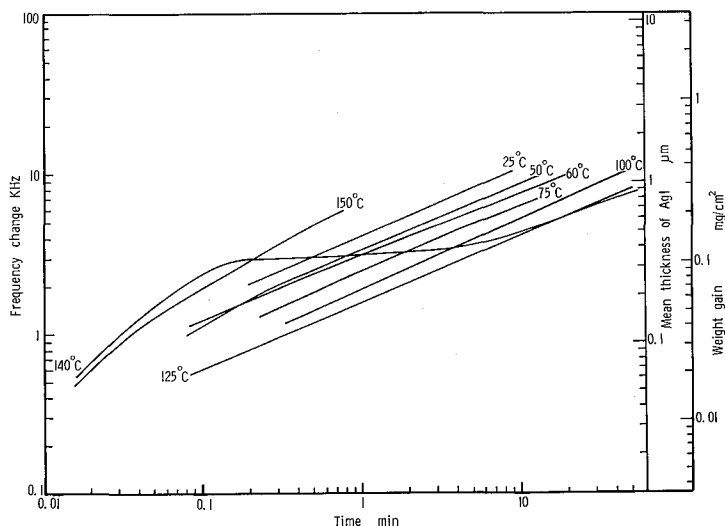


Fig. 1. Double logarithmic plots of weight gain data for the iodination of silver below  $150^\circ\text{C}$  at an iodine pressure of 0.14 Torr.

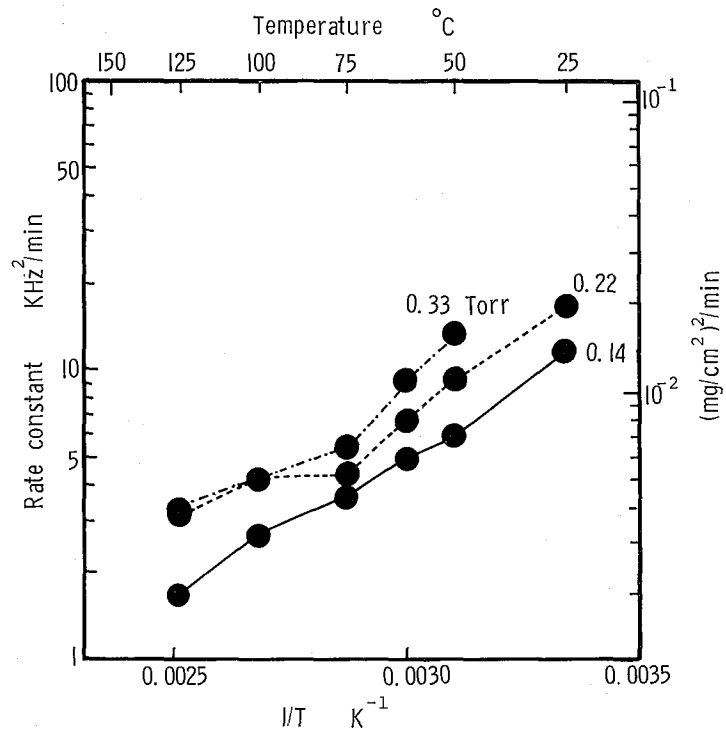


Fig. 2. Temperature dependence of the parabolic rate constant for the iodination of silver in the  $\beta$ -AgI phase region.

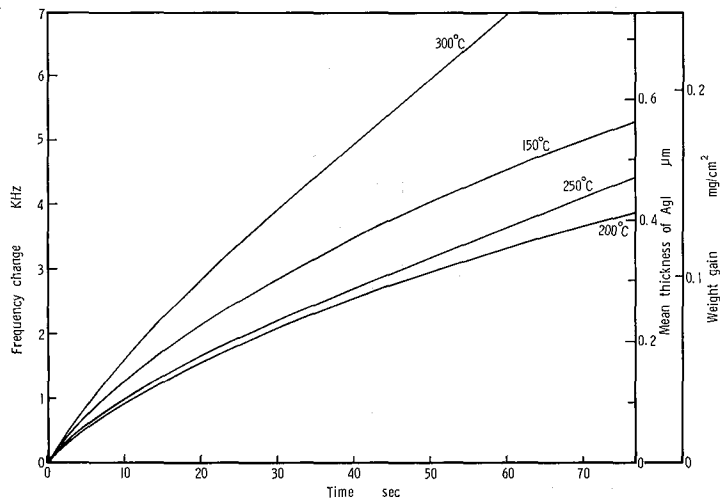


Fig. 3. Weight gain data for the iodination of silver above 150°C at an iodine pressure of 0.051 Torr.

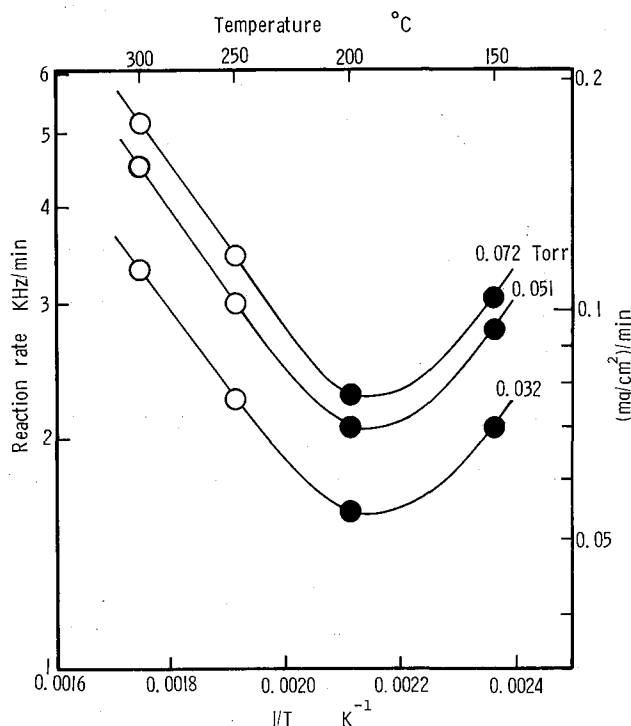


Fig. 4. Temperature dependence of the parabolic (black) and the linear (white) rates at 1 min, for the iodination of silver in the  $\alpha$ -AgI phase region.

Figure 2 shows Arrhenius plots that apply to the reactions for different pressures. The rate constant  $k_p$  was determined for each curve represented by the parabolic relation  $(dm)^2 = k_p t$ , where  $dm$  is weight gain and  $t$  is time. From the plot at 0.14 Torr an activation energy of  $-4.6$  kcal/mol was derived for this parabolic type reaction. The reaction, however, is not due to a simple kinetic process since an activation energy cannot be negative. The rate constants were nearly proportional to the pressure. The gradient of the rate constant/pressure curves became small with increasing temperature.

In the  $\alpha$ -AgI phase region, between 150 and 200°C the reaction rate decreases with increase of temperature, but above 200°C it increases with temperature, as shown in Fig. 3. Below 200°C the reaction follows the parabolic relationship, and above 200°C it follows the linear relationship rather than the parabolic one.

The logarithms of the reaction rates at 1 min are plotted against the inverse of reaction temperature in Fig. 4. The rates are at a minimum near 200°C where the parabolic reaction changes to the linear reaction. The activation energy for the linear reaction above 200°C was roughly estimated from the values at 250 and 300°C to be 5 kcal/mol.

### Reaction of Iodine Vapor with Copper Films

The  $\gamma$ -form (zincblende type) of copper iodide was formed. The results are shown in Fig. 5. Between 25 and 150°C the reaction rate increases with increasing temperature, but above 150°C it decreases with temperature. It is also concluded that the iodination of copper films approximately follows the parabolic rate relationship in the temperature

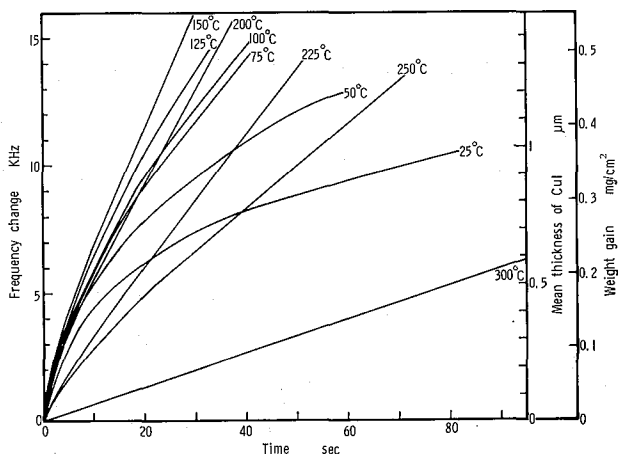


Fig. 5. Weight gain data for the iodination of copper at an iodine pressure of 0.032 Torr.

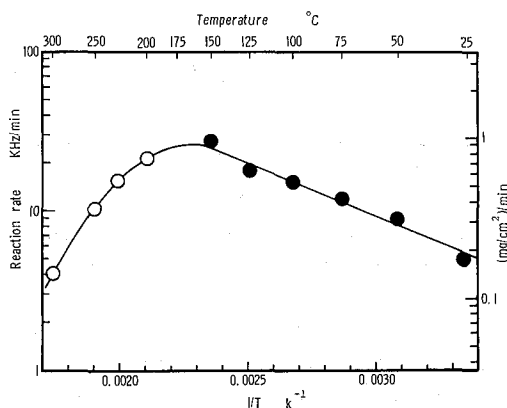


Fig. 6. Temperature dependence of the parabolic (black) and the linear (white) rates at 0.5 min, for the iodination of copper at an iodine pressure of 0.032 Torr.

range 25–150°C and follows the linear rate relationship above 150°C.

The logarithms of the reaction rates at a reaction time of 0.5 min are plotted against the inverse of reaction temperature in Fig. 6. Arrhenius plots of the rate constant  $k_p$  for the parabolic reaction lay on a straight line, like the plots below 150°C in Fig. 6. Thus, the activation energy for the parabolic reaction has been estimated to be 3.9 kcal/mol, and  $k_p$  for the iodination at an iodine pressure of 0.032 Torr is represented as

$$\begin{aligned} k_p &= 7.1 \times 10^4 \exp(-3,900/RT) \text{ KHz}^2/\text{min} \\ &= 85.5 \exp(-3,900/RT) (\text{mg}/\text{cm}^2)^2/\text{min}, \end{aligned}$$

where  $R$  is the gas constant and  $T$  is absolute temperature.

### Reaction of Iodine Vapor with Lead Films

Lead is oxidized even when it is exposed to the air for a very short time. Therefore, whole experiment was carried out under a residual gas pressure less than  $2 \times 10^{-7}$  Torr,

and then the reproducibility of experiments were obtained. The reaction product was lead iodide ( $\text{PbI}_2$ , hexagonal) crystals. The weight gain data are reproduced in Fig. 7. The reaction approximately obeys the parabolic rate relationship, and its rate increases with increasing temperature. The experiments were performed at iodine pressures of 0.08, 0.13, 0.21, and 0.41 Torr, and a definite difference could not be recognized among the data at the same temperature.

Figure 8 shows an Arrhenius plot that applies to this reaction. The rate constant

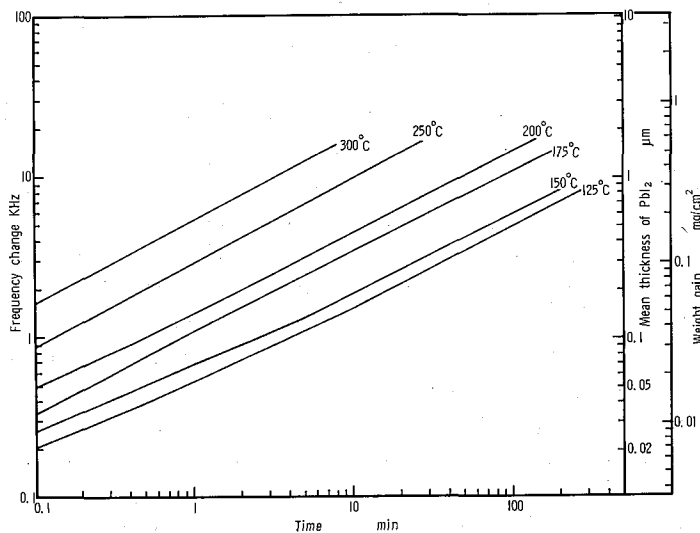


Fig. 7. Double logarithmic plots of weight gain data for the iodination of lead at an iodine pressure of 0.21 Torr.

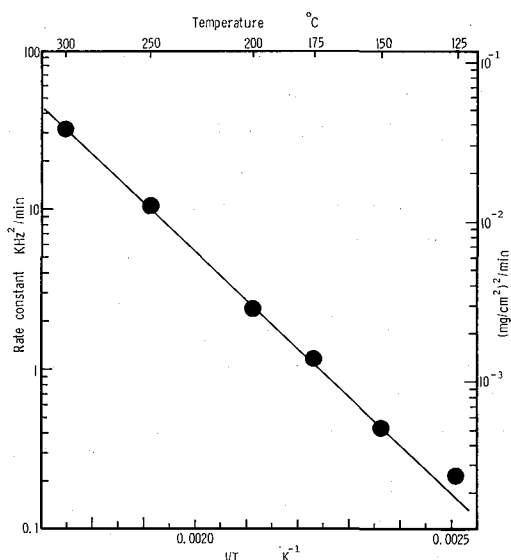


Fig. 8. Temperature dependence of the parabolic rate constant for the iodination of lead at an iodine pressure of 0.21 Torr.

$k_p$  is represented as

$$\begin{aligned} k_p &= 6.41 \times 10^6 \exp(-13,900/RT') \text{ KHz}^2/\text{min} \\ &= 77 \times 10^2 \exp(-13,900/RT) (\text{mg}/\text{cm}^2)^2/\text{min}. \end{aligned}$$

The iodination below 100°C was still influenced by a little surface oxidation owing to the residual gas, and then it showed the poor reproducibility. The reaction rates slowed down, especially for an initial few minutes, and the reaction could not be represented by a simple rate equation.

#### IV. DISCUSSION

The present results for the iodination of silver, copper, and lead are not in agreement with the early measurements of Tammann and Köster<sup>2)</sup> who reported the independence of reaction rate from temperature. The abnormal reactions which do not obey Arrhenius's equation took place in some temperature ranges. The observed reaction formulas and the formed crystals are summarized in Table I. The iodinations of silver, copper, and lead are not similar in occurrence of the abnormal reaction, and it is still difficult to give general explanation to the reaction mechanism of iodine with metals.

It has been reported<sup>16)</sup> that the  $\beta$ -AgI film is a metal excess semiconductor like ZnO crystal since the electrical conductivity of a similar AgI film decreased with increasing iodine pressure. When a metal is oxidized according to the Wagner mechanism<sup>5,8)</sup> and a metal excess semiconductor forms, the oxidation rate is determined by diffusion of metal ions and nearly independent of the partial pressure of oxygen. However, since the observed growth rate of the  $\beta$ -AgI films increased nearly in proportion to iodine pressure, the diffusion of the silver ions may not be dominant in this reaction. Evans and Bannister<sup>3)</sup> assumed that iodine moves inwards through pores of a few molecular diameter in loose union with silver iodide at the iodination of silver immersed in a solution of iodine. This is acceptable for the present reaction; the diffusion of iodine through the iodide film is dominant rather than that of silver ions and rate-determining this parabolic reaction. Crystal grain boundaries along which the mobility of atoms is greater may correspond to the pores. The diffusion of iodine may be influenced by the number of adsorbed iodine

Table I. Iodination-time relationships and formed crystals at various temperatures.

Metal \ Temp	25°C	150°C	200°C	300°C
Silver	<div> <div>Parabolic (abnormal)</div> <div><math>\beta</math>-AgI</div> </div>	<div> <div>Parabolic (abnormal)</div> <div>*</div> </div>	<div> <div>Linear (5 kcal/mol)</div> <div><math>\alpha</math>-AgI</div> </div>	
Copper	<div> <div>Parabolic (3.9 kcal/mol)</div> <div></div> </div>	<div> <div>*</div> <div><math>\gamma</math>-CuI</div> </div>	<div> <div>Linear (abnormal)</div> <div></div> </div>	
Lead	<div> <div>Parabolic (13.9 kcal/mol)</div> <div></div> </div>	<div> <div>Parabolic (13.9 kcal/mol)</div> <div>PbI<sub>2</sub></div> </div>		



atoms on the iodine-iodide interface. If we assume a heat of adsorption of 9 kcal/mol which is a possible value for the gas consisting of heavy molecules, then the decrease of the adsorbed atoms is about 50-fold between 25 and 125°C.<sup>17)</sup> The decrease of the adsorbed iodine atoms may reduce the concentration gradient of iodine atoms through the iodide film and thus may retard this reaction by overcoming the effect of the ordinary diffusion coefficient increasing with temperature. The number of adsorbed atoms increases as the iodine pressure is raised, which may cause the observed increment of the reaction rate. Thus, the adsorption of iodine on the film surface seems to play an important role in this reaction. An X-ray diffraction study revealed that the  $\beta$ -AgI crystals had a strong tendency to grow with their basal planes parallel to the surface as the reaction temperature was raised. The matching among the crystals successively grown with the same orientation is so good that iodine can move less easily through the close-fitting iodide film. This may be another reason for the observed decrease in the reaction rate with increasing temperature.

The iodination below 200°C in the  $\alpha$ -AgI phase region was very similar to that in the  $\beta$ -AgI phase region. However, since silver atoms are able to wander in a fluid state throughout the  $\alpha$ -AgI structure, the diffusion of silver may be predominant and may be rate-determining this parabolic reaction. The adsorption of the iodine gas and the structure of the  $\alpha$ -AgI films may influence the diffusion to lead to cause the observed temperature dependence of the reaction.<sup>12)</sup> As the temperature is much raised, the change of the film structure and the decrease of adsorbed atoms become so small that an increase of the ordinary diffusion coefficient may overcome their effects. Above 200°C, the diffusion is no longer rate-determining process and the linear reaction prevails, in which a phase boundary reaction is rate-determining. The following processes can be considered as possible mechanisms of the phase boundary reaction; chemisorption of iodine atoms and the introduction of chemisorbed ions in the iodine-iodide phase boundary, transfer of silver atoms from the metal phase into the iodide lattice, and nucleation and growth of iodide crystals.<sup>7)</sup>

The parabolic iodination of copper below 150°C had a very small activation energy of 3.9 kcal/mol. The adsorption of iodine causes cuprous ions and electrons to migrate to the surface and the CuI lattice to extend, leaving the vacancies in the cuprous ion lattice and a defect of electrons.<sup>5,6)</sup> The concentration of vacancies of the cuprous ions, whose diffusion is considered to be rate-determining for this parabolic reaction, decreases with increasing temperature.<sup>15,18)</sup> Thus, the decrease of the vacancy concentration acts on the reaction rate to slow down with increase of temperature, and may lead to the very small activation energy.

A phase boundary reaction can be assumed to be the rate-determining factor in the iodination of copper above 150°C. The decrease of the adsorbed atoms is about 5-fold between 200 and 300°C for a heat of adsorption of 9 kcal/mol, and this is in good agreement with the observed decrease of the reaction rate. Thus, it is concluded that the most probable mechanism is the chemisorption of iodine atoms and the introduction of chemisorbed ions in the gas-iodide interface.

The conduction mechanism of lead iodide is very complicated because both lead and iodine ions participate in conduction.<sup>8)</sup> Since the ionic conduction is predominant in any case and since parabolic rate behavior was observed, it can be concluded that

electronic conduction through the lead iodide layer is the rate-determining step of the iodination process.

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